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Removal of methylene blue dye from aqueous solutions by a new chitosan/zeolite composite from shrimp waste: Kinetic and equilibrium study

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Abstract−The adsorption of methylene blue dye (MBD) from aqueous solutions was investigated using a new composite made up of shrimp waste chitosan and zeolite as adsorbent. Response surface methodology (RSM) was used to optimize the effects of process variables, such as contact time, pH, adsorbent dose and initial MBD concentration on dye removal. The results showed that optimum conditions for removal of MBD were adsorbent dose of 2.5 g/L and pH of 9.0, and initial MBD concentration of 43.75 mg/L and contact time of 138.65 min. The initial concentration of dye had the greatest influence on MBD adsorption among other variables. The experimental data were well fitted by the pseudo-second order kinetic model, while the Freundlich isotherm model indicated a good ability for describing equilibrium data. According to this isotherm model, maximum adsorption capacity of the composite was 24.5 mg/g. Desorption studies showed that the desorption process is favored at low pH under acidic conditions.

Keywords: Methylene Blue Dye, Shrimp Wastes, Chitosan, Zeolite

INTRODUCTION

Many industries, such as those producing pulp and paper, textile, food, cosmetics, leather, paint, ceramic, plastics, dyestuffs and pottery, use dyes to color their products [1-15], a relevant portion of which is lost during manufacture [16-18]. Many dyes are difficult to degrade due to their recalcitrant and non-biodegradable nature and stability toward oxidizing agents, heat and light [2,5]. Methylene blue, a common basic dye, is mainly used by textile industry to color wood, cotton and silk, but it can be harmful to the eyes of humans and animals. In addition, MB may lead to breathing problems, gastritis, nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [10]. The resulting colored wastewater becomes impenetrable to sunlight, thus affecting photosynthetic microorganisms and aquatic plants, and interfering with the ecology of the receiving water body [19]. The main treatment methods for dye removal are membrane, electrochemical [20], coagulation/flocculation [21], biological decomposition [22], ion exchange [23], ozonation [24], photo-degradation [25] and adsorption [26-28] technologies.

Among them, adsorption has peculiar advantages such as low cost, simplicity of design and operation, large sorbent availability, ability to treat dye at high concentration, insensivity to toxic substances and high effectiveness [2,19]. Recently, there has been a growing interest in biosorbents such as chitosan, a liner polysaccharide and second-most abundant biopolymer in nature [29,30], which is produced by chitin deacetylation. Great attention has been paid to chitosan as an adsorbent for effective removal of dyes, fluoride, nitrate and heavy metals [30]. Despite abundant usage of chitosan in the removal of different pollutants, it is very sensitive to pH, being soluble in acidic media [29,30]. To overcome this drawback, different substances such as hydroxyapatite [31], sand [32], bentonite [33], attapulgite [34], fly ash [4], activated clay [35], montmorillonite [36], perlite [37] and granular activated carbon [38] have been successful in forming composites with chitosan with high adsorption capacity and resistance to acidic environment [30,39]. Natural zeolite, provided with a three-dimensional framework structure, is an abundant, low cost, chemically and mechanically stable [30] attractive material that may alternatively be used to form composites with chitosan. Such chitosan/zeolite composites have been successfully used to remove heavy metal ions from aqueous solutions [30].

Many researchers have investigated dye adsorption onto different adsorbents in batch systems [2-8,10-12,18]. In classic sorption studies, optimization is performed by varying one parameter at a time, keeping the other parameters constant. But this approach is laborious and time consuming, requiring a large number of experiments [1,40]. Other shortcomings associated with conventional

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methods are non-reliability of results and lack of ability to predict the combined effects of independent variables on response at a time [1]. All these drawbacks can be solved by statistical experimental designs combined with response surface methodology (RSM), which consists of a group of mathematical and statistical techniques able to optimize the process variables collectively influencing a response [40]. Although a chitosan/zeolite composite was used to remove an anionic dye from aqueous solution by Nešić et al. [41], to the best of our knowledge, this is the first report on RSM optimization of dye adsorption using chitosan/zeolite composite.

Based on this background, our aims were the a) preparation and characterization of chitosan/zeolite composites, b) study of the adsorption of methylene blue dye (MBD) on a chitosan/zeolite composites in batch experiments, c) investigation of the effects of initial MBD concentration, pH, contact time and adsorbent dosage on dye removal, d) optimization of experimental conditions using a central composite design combined with RSM, e) fitting the experimental data of adsorption capacity with different kinetic (pseudo-first order, pseudo-second order and intraparticle diffusion) models and isotherms (Langmuir and Freundlich) models, and f) study on the recovery and recycling of the prepared adsorbent.

MATERIALS AND METHODS

1. Materials

Analytical grade hydrochloric acid, sodium hydroxide, methylene blue dye (MBD) were purchased from Merck (Darmstadt, Germany). Natural zeolite was purchased from Negin Powder Company (Semnan, Iran) and sieved to obtain particle size less than 150 μm. Shrimp waste (SW) was obtained from local markets (Mashhad, Iran), washed to remove loose tissue and adhering dirt and then dried in sunlight for 1-2 day. The chemical structure of MBD is illustrated in Fig. 1. Standards and solutions were prepared using double distilled water.

2. Preparation of Raw Chitosan

Raw chitosan was prepared by the method described by Sagheer et al. [42] with some modification. Briefly, to obtain chitin, dried SW was fed into a grinder, ground and submitted to successive steps of demineralization, deproteinization, and deacetylation. Demineralization and subsequent deproteinization were carried out at a ratio of 1 : 20 (w/v) for 24 h at room temperature using 1.0 M HCl and 1.0 M NaOH, respectively. Chitin deacetylation to chitosan was done using 50% NaOH at a ratio of 1 : 20 (w/v) for 2 h at 100 °C. The resulting solids fraction was filtered and then washed with distilled water up to neutral pH and dried at room temperature for 24 h. Finally, the residue was dried in an oven at 60 °C for 4 h and then stored for further use.

3. Chitosan/Zeolite Composite Preparation

Chitosan/zeolite composite (CZC) was prepared according to Lin and Zhan [30]. To this purpose, 8.0 g of raw chitosan prepared as described in the previous section was dissolved in 400 mL of 2% (v/v) acetic acid, while 40.0 g of clinoptilolite was suspended in 400 mL of distilled water and stirred for 30 min. After addition of chitosan solution to zeolite suspension and stirring for 1.5 h, the system pH was adjusted to 9.0 by addition of 2.0 M NaOH. Then, the settled CZC was washed with distilled water until reaching neutral pH and dried at 105 °C.

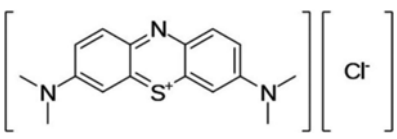

Fig. 1. The chemical structure of Methylene Blue Dye.

Table 1. Physicochemical properties of raw chitosan

Property	Value	Unit
Yield	16.6	% (w/w)
Moisture content	5.2	% (w/w)
Ash content	0.4	% (w/w)
Degree of acetylation	17.9	%
Water binding capacity	329.6	%

4. Characterization of Raw Chitosan and Chitosan/Zeolite Composite

Chitosan was physicochemically characterized by determination of yield, moisture and ash content, degree of acetylation and water binding capacity according to standard protocols [43], whose results are listed in Table 1. To investigate the change of functional groups in the CZC samples before and after MBD adsorption, Fourier-transform infrared (FTIR) analysis was performed by a Nicolet, model Avatar 370 FTIR (Thermo Electron Scientific Instruments, Madison, WI, USA), in the range of 400-4,000 cm^{-1} with a resolution of 4 cm^{-1} and 16 scans. Microscopic characterization was performed using a scanning electron microscope (SEM), model LEO-1450 VP (Zeiss, Oberkochen, Germany), to observe the surface microstructure of the prepared adsorbent. The elemental analysis of adsorbent before and after adsorption was performed using energy-dispersive X-ray spectrometer (EDX, SAMx, Germany).

5. Design of Experiments

A central composite design (CCD) combined with response surface methodology was employed to design the set of adsorption experiments through which to investigate the effects of the main independent variables, namely, contact time, solution pH, adsorbent (CZC) dosage and MBD initial concentration, on MBD removal selected a response. Such an approach has extensively been used to optimize dye removal with various adsorbents [1,40]. For n independent variables, a typical CCD consists of 2^n factorial runs with $2n$ axial runs and n_c center runs; therefore, the total number of experiments required for optimization, can be calculated by the equation [44]:

$$N=2^n+2n+n_c \quad (1)$$

being in the present case $N=2^4+2\times4+6=30$

To optimize the adsorption process, the following quadratic equation model was used [40,44]:

$$y=b_0+\Sigma_{i=1}^{4}b_i x_i+\Sigma_{i=1}^{4}\Sigma_{j=1}^{4}b_{ij}x_i x_j+\Sigma_{i=1}^{4}b_{ii}x_i^2 \quad (2)$$

where y is the response variable (MBD removal, %), x_i and x_j are the independent variables, b_0 is the model constant; b_i is the linear coefficient, b_{ii} is the quadratic coefficient, and b_{ij} is the interaction

Table 2. Conditions and results of designed experiments of methylen blue dye (MBD) adsorption onto chitosan/zeolite composite

Run	Contact time (min)	pH	Adsorbent dosage (g/L)	Initial MBD concentration (mg/L)	MBD removal (%)
1	97.50	7.0	2.0	62.50	43.7
2	56.25	5.0	1.5	81.25	30.1
3	97.50	7.0	2.0	62.50	43.0
4	97.50	7.0	2.0	62.50	44.9
5	97.50	7.0	2.0	25.00	95.0
6	97.50	11.0	2.0	62.50	67.6
7	15.00	7.0	2.0	62.50	33.4
8	56.25	5.0	1.5	43.75	45.4
9	138.75	9.0	1.5	43.75	61.6
10	56.25	9.0	2.5	81.25	47.2
11	138.75	9.0	2.5	81.25	51.4
12	97.50	7.0	2.0	62.50	42.9
13	56.25	9.0	2.5	43.75	75.5
14	138.75	9.0	1.5	81.25	32.6
15	97.50	7.0	2.0	62.50	43.3
16	97.50	7.0	3.0	62.50	54.8
17	180.00	7.0	2.0	62.50	49.5
18	138.75	5.0	1.5	43.75	50.0
19	56.25	5.0	2.5	43.75	78.9
20	138.75	5.0	1.5	81.25	31.7
21	97.50	7.0	2.0	100.00	44.7
22	56.25	9.0	1.5	81.25	38.0
23	138.75	5.0	2.5	43.75	74.4
24	97.50	7.0	2.0	62.50	42.6
25	97.50	7.0	1.0	62.50	26.3
26	56.25	5.0	2.5	81.25	44.5
27	97.50	3.0	2.0	62.50	45.8
28	138.75	5.0	2.5	81.25	49.3
29	138.75	9.0	2.5	43.75	84.9
30	56.25	9.0	1.5	43.75	47.6

coefficient. The contact time, solution pH, adsorbent dosage and initial MBD concentration (independent variables) were varied in the ranges 15.00-180.00 min, 3.0-11.0, 1.0-3.0 g/L and 25.00-100.00 mg/L, respectively. Analysis of variance (ANOVA) was used to model and optimize the output response as well as to estimate the statistical parameters. The conditions and results of designed experiments suggested by Design Expert 7.1 Software are summarized in Table 2.

6. Adsorption Experiments

6-1. Kinetic and Equilibrium Study

A kinetic study was performed under optimized conditions of adsorbent dosage (2.5 g/L) and pH (9.0) to evaluate the mechanism of solute removal and to determine the kinetic parameters for designing a continuous reactor [1-3]. To this purpose, 0.25 g of CZC was added to 100 mL of MDB solutions with initial dye concentration in the range 25.00-100.00 mg/L at pH 9. The solutions were shaken at 200 rpm at room temperature, and samples were taken at given time intervals and centrifuged at 4,000 rpm for 10 min. Residual MBD concentration in the centrifuged samples was determined by UV-visible spectrophotometer, model T80+ (PG instrument Ltd., Leicester, UK), at 670 nm.

To determine MBD adsorption capacity of CZC, an equilibrium study was also performed varying initial dye concentration, pH and adsorbent dosage. The MBD adsorption capacity per unit mass of CZC at equilibrium, q_e (mg g^{-1}), was calculated by the equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where C_0 and C_e are the initial concentration of dye and that at equilibrium (mg/L), respectively, V the solution volume (L) and m the mass of added CZC (g).

6-2. Kinetic Models

Experimental data of methylene blue dye adsorption onto chitosan/zeolite composite along the time were analyzed by linearized forms of the three most common adsorption kinetic models:

a) The pseudo-first order rate equation of Lagergren [45]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where q_t (mg/g) is the dye sorption capacity of CZC after a time t (min) and k_1 the pseudo-first order rate constant (min^{-1}).

b) The pseudo-second order model of Ho and McKay [46]:

$$\frac{t}{q_t}=\frac{1}{k_2 q_e^2}+\frac{t}{q_e} \quad (5)$$

where k_2 is the second order rate constant (g mg^{-1} min^{-1}), which can be calculated from the slope of the straight line obtained by plotting t/q_t versus t;

c) The intraparticle diffusion model [47]:

$$q_t=k_p t^{0.5}+C \quad (6)$$

where C (mg/g) is a parameter related to the boundary layer thickness, k_p (mg g^{-1} $min^{-0.5}$) is the intraparticle diffusion rate constant, which can be calculated as the slope of the straight line obtained by plotting q_t versus $t^{0.5}$.

6-3. Isotherm Models

The well-known isotherm models of Langmuir and Freundlich have been tested to analyze the experimental data of adsorption isotherms. The Langmuir isotherm model, which is based on the assumption that the adsorption takes place at specific homogenous sites onto a monolayer adsorbent surface, can be described in its linearized form as:

$$\frac{C_e}{q_e}=\frac{1}{K_L Q_0}+\frac{1}{Q_0}C_e \quad (7)$$

where Q_0 and K_L are the maximum capacity of adsorption (mg/g) and Langmuir constant (L/mg) related to adsorption energy.

The dimensionless separation or equilibrium factor (R_L), which is defined by the equation:

$$R_L=\frac{1}{1+K_L C_0} \quad (8)$$

is an additional parameter linked to the Langmuir isotherm model [3,39], whose value indicates whether adsorption is unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($R_L<1$) or irreversible ($R_L=0$) [2,3].

On the other hand, the Freundlich isotherm model assumes that the adsorption has a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface [7]. The linear form of Freundlich isotherm model can be expressed as:

$$\mathrm{Log}q_e=\mathrm{Log}K_F+\left(\frac{1}{n}\right)\mathrm{Log}C_e \quad (9)$$

where K_F and 1/n are Freundlich constant ($mg^{1-1/n}$ $L^{1/n}$ g^{-1}) related to sorbent sorption capacity and 1/n a dimensionless empirical parameter depending on sorption intensity and indicating whether sorption is unfavorable (1/n>1), favorable (0<1/n<1) or irreversible (1/n=0) [2,3].

6-4. Desorption Study

To carry out the desorption study, 10.0 g of CZC were added to 0.5 L of MBD solution with initial dye concentration of 500 mg/L and mixed at 200 rpm for 24 h at room temperature until equilibrium was reached. After that, the adsorbent was separated from solution by centrifugation and then dried. 0.25 g of the MBD-bound CZC was transferred to clean Erlenmeyer flasks containing 100 mL of diluted HCl or NaOH solutions with different pH values (5.0, 7.0 or 9.0) until reaching a new equilibrium. The adsorbent obtained under this condition was used in resorption studies.

RESULTS AND DISCUSSION

1. Characterization of Adsorbents

The FTIR spectra of chitosan, zeolite, chitosan/zeolite composite (CZC) and MBD-bound CZC are shown in Fig. 2. The major bands for chitosan can be assigned as follows: 3,447.59 cm^{-1} (NH_2

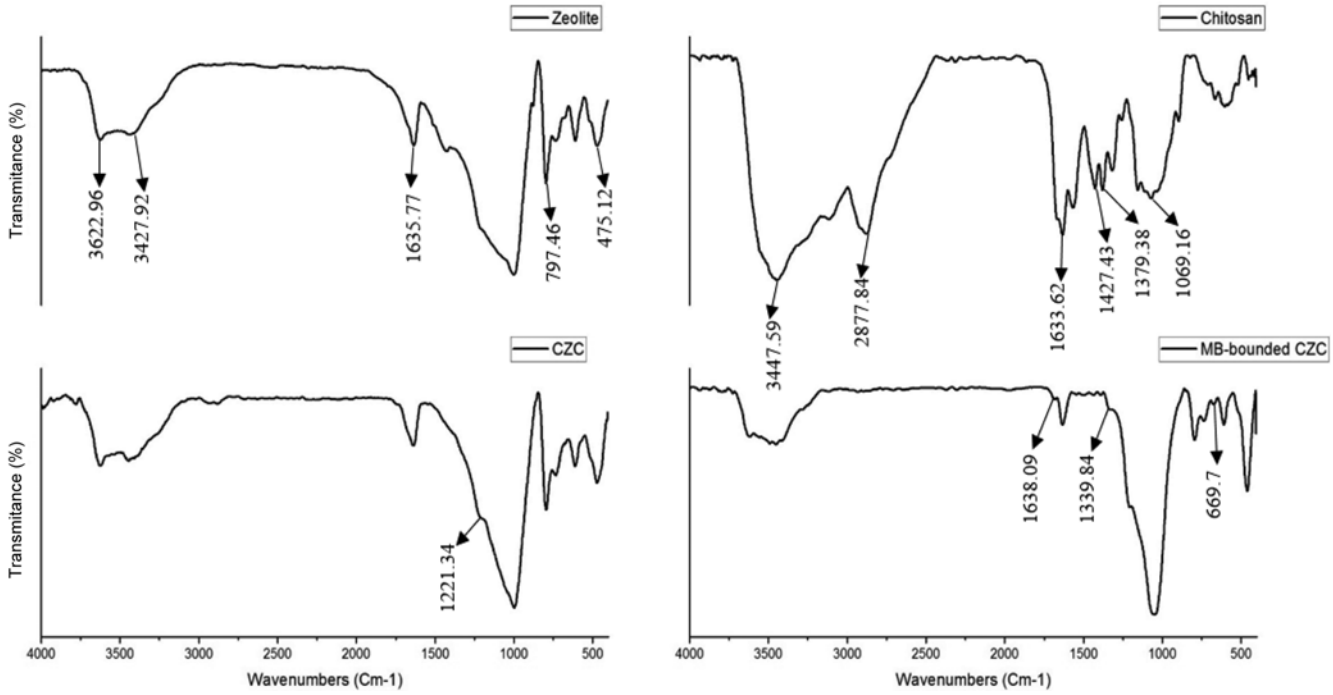

Fig. 2. FT-IR spectra of chitosan/zeolite composite (CZC), zeolite (Z), chitosan (CH) and MBD-bound CZC.

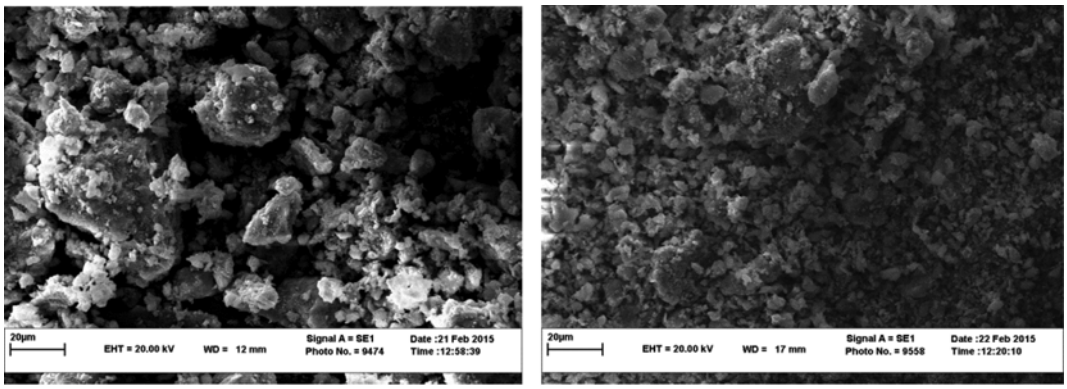

Fig. 3. SEM images of (a) chitosan/zeolite composite (CZC) and (b) MBD-bound CZC.

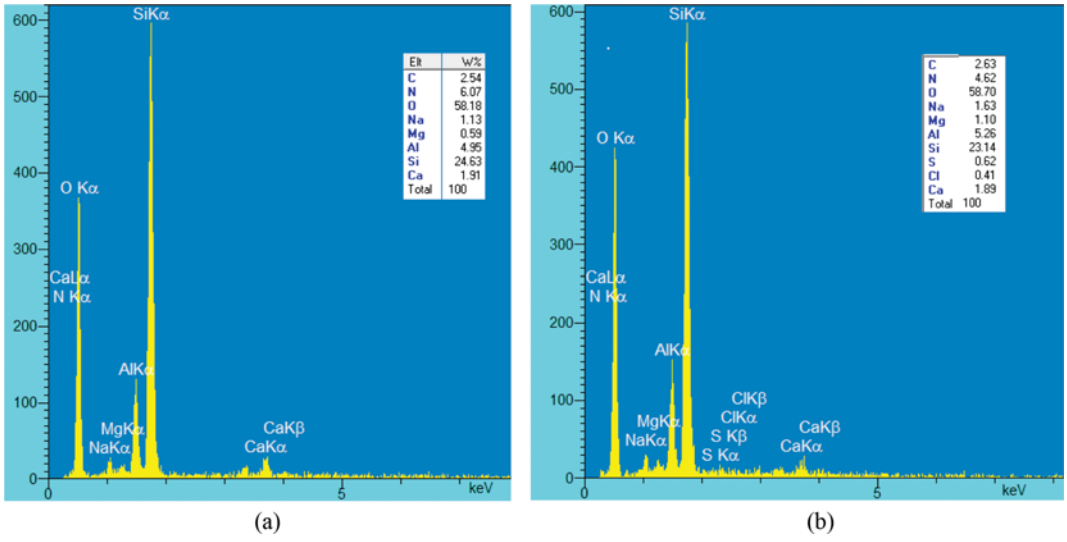

Fig. 4. EDX analysis of (a) chitosan/zeolite composite (CZC) and (b) MBD-bound CZC.

and OH groups stretching vibration), 2,877.84 cm^{-1} (-CH stretching vibration), 1,633.62 cm^{-1} (N-H bending vibrations of NH_2 group), 1,427.43 cm^{-1} (C-O bending vibration), 1,379.38 cm^{-1} (-CH symmetric bending vibration), and 1,069.16 cm^{-1} (-CO stretching vibration in -COH). On the other hand, the major absorption bands for zeolite in the region 1,600-3,700 cm^{-1}, namely 3,622.96, 3,427.92, 1,635.77 cm^{-1}, can be assigned to the presence of zeolitic water [30], while that observed at 1,000.14 cm^{-1} to stretching vibration of Si-O [48] and those at 797.46 and 475.12 cm^{-1} to quartz or amorphous SiO_2 stretching vibration and Si-O-Si bending mode [30]. Compared to the spectrum of natural zeolite, that of CZC exhibits an additional absorption band at 1,221.34 cm^{-1}, which may be a proof of the combination of natural zeolite and chitosan. Adsorption of MBD onto CZC led to the appearance of new peaks at 1,683.09, 1,339.84 and 669.69 cm^{-1}, as well as shifts of the above-identified peaks to 3,615.89, 3,450.1, 1,633.38, 1,200.91, 1,047.12, 735.07 and 461.28 cm^{-1}, respectively, as the likely result of MBD interaction with functional groups present on CZC surface.

The scanning electron microscope (SEM) images of CZC and MBD-bound CZC (Fig. 3) reveal that CZC surface is characterized by a porous and non-smooth texture, which was partially lost after MBD removal, hence suggesting uneven and abundant adsorption of dye onto the whole sorbent surface.

Energy-dispersive X-ray spectroscopy of CZC before and after dye adsorption (Fig. 4) demonstrated that C, N, O, Al and Si are major elements in the adsorbent with weight percents of 2.54%, 6.07%, 58.18%, 4.95%, 24.63%, respectively. The presence of S and Cl in EDX mapping of CZC after dye adsorption confirmed dye adsorption by CZC.

2. Effect of Independent Variables on MBD Removal

2-1. Effect of Contact Time and Adsorbent Dosage

Fig. 5 shows the combined effect of contact time and adsorbent dosage on MBD removal by CZC at constant pH 7 and initial dye concentration of 62.5 mg/L. One can see that both independent variables positively influenced the selected response, in that it increased with increasing both. For instance, at the highest adsorbent dosage (2.5 g/L), a former phase of very fast adsorption during which MBD removal increased up to 48% within 30 min (results not shown) was followed by a latter slow adsorption phase, achieving 56% removal after no less than 180 min (Fig. 5). Such a two-phase

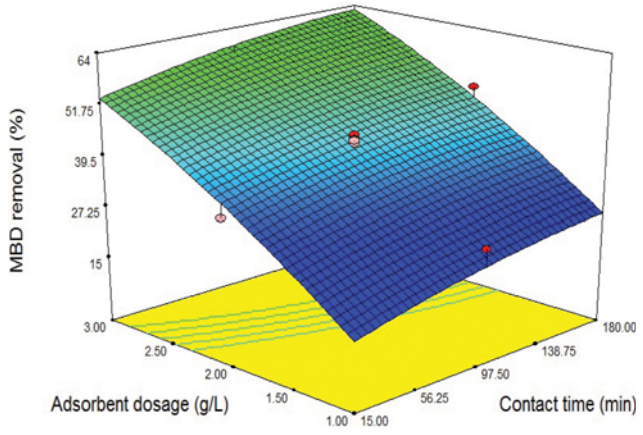

Fig. 5. Combined effect of contact time and adsorbent dosage on MBD removal (pH=7, Initial dye concentration=62.5 mg/L).

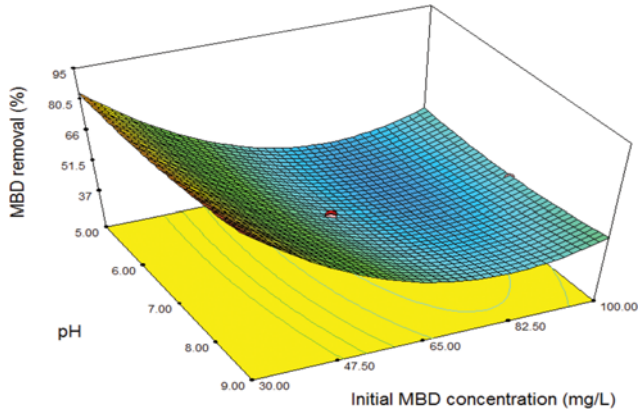

Fig. 6. Combined effect of initial MBD concentration and pH on MBD removal (contact time=97.5 min, adsorbent dosage= 2 g/L).

behavior is in agreement with that observed in other studies [40]. On the other hand, it is obvious that MBD removal increased with adsorbent dosage, because of greater availability of surface area and adsorption sites on adsorbent.

2-2. Effect of pH and Initial MB Concentration

The pH of aqueous medium is one of the parameters mostly influencing the adsorption process through a combination of various mechanisms such as protonation/deprotonation of dyes and adsorbent surface [11]. The simultaneous effects of pH and initial dye concentration on MBD removal by CZC are shown in Fig. 6. One can see that a progressive alkalization of the medium had a positive effect on such a response. For instance, at an initial dye concentration of 30.00 mg/L, it increased from about 80 to 94% when the solution pH was raised from 5.0 to 9.0. This behavior should be ascribed to the CZC point of zero charge (pH_{pzc}), i.e., the pH value at which sorbent surface does not carry charges, that was found to be 7.4. At pH>7.4, the CZC surface was negatively charged, and the cationic dye sorption was enhanced by the electrostatic attraction between them, whereas, at pH<7.4, the CZC surface was positively charged, thereby affecting MBD adsorption capacity of CZC due to the cationic nature of both sorbent and sorbate [30]. That being so, maximum MBD removal occurred at pH 9.0. Therefore, subsequent kinetic and isotherm experiments were conducted just at such an optimum pH value.

According to the same figure, removal efficiency decreased considerably with increasing dye concentration, because of the corresponding decrease in the ratio of the number of available active sites to that of dye molecules [12]. For instance, at the optimum pH (9.0), an increase in the initial MBD concentration from 30.00 to 100.00 mg/L led to a decrease in the removal efficiency from 94 to no more than 42%, which confirms how much the adsorption process is influenced by the initial sorbate concentration.

3. Adsorption Kinetics

The values of kinetic parameters estimated fitting the experimental values of dye sorption capacity of CZC along the time (q_t) by the selected kinetic models are listed in Table 3. For various initial concentrations of MBD, the pseudo-second order model (Eq. (5)) proved to be the best fitting model, for it provided the highest determination coefficients ($R^2 \geq 0.996$) compared with the others. In addition, the values of dye sorption capacity of CZC at equilibrium ($q_{e,est}$) estimated by this model did not differ more than ±7.6% from the experimental ones ($q_{e,ex}$). These results suggest that MBD adsorption by CZC took place via a chemisorption mechanism involving valence forces by sharing or electrons exchange between sorbate and sorbent [40].

Nonetheless, the satisfactory R^2 values of fitting with the intraparticle diffusion model ($0.800 \leq R^2 \leq 0.975$) as well as the positive values of the parameter related to the boundary layer thickness (C), which progressively increased from 8.71 to 19.23 mg/g with increasing the initial MBD concentration from 25.00 to 100.00 mg/L, suggest that intraparticle diffusion may have been the rate-controlling

Table 3. Kinetics constants of MBD adsorption onto Chitosan/zeolite composite at different initial MBD concentrations (pH=9, solution volume=100 mL, adsorbent dosage=2.5 g/L)

MBD concentration (mg/L)	$q_{e,ex}$ (mg/g)	Pseudo-first order model			Pseudo-second order model			Intraparticle diffusion model		
		k_1 (min^{-1})	$q_{e(est)}$ (mg/g)	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e,est}$ (mg/g)	R^2	k_P (mg g^{-1} $min^{-0.5}$)	C (mg/g)	R^2
25.00	8.93	0.017	0.14	0.593	0.241	8.99	0.999	0.024	8.71	0.800
50.00	14.50	0.029	1.20	0.989	0.137	14.39	0.999	0.156	13.11	0.975
75.00	20.95	0.014	2.94	0.776	0.049	20.12	0.996	0.392	16.79	0.845
100.00	23.04	0.082	7.40	0.800	0.021	23.75	0.997	0.501	19.23	0.925

$q_{e(ex)}$=experimental value of MBD adsorption capacity of CZC; $q_{e(est)}$=value of MBD adsorption capacity of CZC estimated by the model

Table 4. Constants of Langmuir (K_L) and Freundlich (K_F) isotherm models applied to MBD adsorption onto chitosan/zeolite composite and related determination coefficients

Langmuir isotherm			Freundlich isotherm						
Q_0 (mg/g)	K_L (L/mg)	R^2	K_F ($mg^{1-1/n}\ L^{1/n}\ g^{-1}$)	1/n (dimensionless)	R^2	R_L (dimensionless)			
						Concentration (mg/L)			
						25	50	75	100
24.51	0.303	0.956	8.822	0.264	0.999	0.116	0.061	0.042	0.032

Table 5. Adsorption capacity of low cost adsorbents for MBD removal

Adsorbent	MBD adsorption capacity (mg/g)	Initial MBD concentration (mg/L)	pH	Adsorbent dosage	Contact time (min)	MBD removal percent (%)	Reference
Charred citrus fruit peel	25.5	30	7.0	0.48 g	-	98	Dutta et al. [40]
Charred parthenium	98.06	25	7.0	0.22 g	-	93.4	Chatterjee et al. [1]
Millet	3.745-4.739	6	6.0	0.25 g	-	99	Ghaedi et al. [49]
Cogongrass	27.4	100	9.0	1.0 g	40	99.09	Su et al. [50]
cashew nut shell	68.72	-	9.0	-	90	-	Kumar et al. [19]
Chitosan/zeolite composite	24.5	43.75	9.0	0.25	138.65	84.85	This study

step of the sorption process [2,3,40].

4. Adsorption Isotherms

The applicability of the Langmuir and Freundlich isotherms to MBD adsorption onto CZC was studied by plotting C_e/q_e versus C_e and ln q_e against ln C_e respectively. As shown in Table 4, where the parameters estimated by fitting the experimental equilibrium data by both models are summarized, the Freundlich isotherm exhibited better fitting (R^2=0.999) than the Langmuir one (R^2=0.956). Moreover, values of the separation factor (R_L) in the range from zero to one and decreasing with increasing the initial dye concentration point out that MBD adsorption by CZC was a favorable process at low initial dye concentrations.

According to Langmuir model, maximum MBD adsorption capacity of CZC was found to be 24.5 mg/g, a value comparable with those of some other adsorbents such as charred citrus fruit peel (25.5 mg/g) [40] and cogongrass (27.4 mg/g) [50] (Table 5).

5. Optimization of MBD Removal

RSM was used to optimize the selected independent variables, viz. contact time, initial dye concentration, pH and adsorbent dosage, i.e., to find their optimum values able to maximize MBD removal selected as a response. To consider the combined effects of these variables in their coded form (x_1=contact time; x_2=pH; x_3=adsorbent dosage; x_4=initial dye concentration), the second-order equation (Eq. (10)) suggested by the software was applied to the experimental values of MBD removal, which provided the values of coefficients listed in the third column of Table 6.

$$\begin{aligned}\text{MBD removal}(y) = {} & +43.40+2.54\times X_1+3.25\times X_2+9.41\ X_3 \\ & -12.25\times X_4+0.98\times X_1X_2-0.55\times X_1X_3 \\ & -1.14\times X_1X_4-0.67\times X_2X_3-0.47\times X_2X_4 \\ & -3.07\times X_3X_4-0.39\times X_1^2+3.42\times X_2^2-0.6\times X_3^2+6.70\times X_4^2\end{aligned} \quad (10)$$

The results of ANOVA summarized in the same table indicates that the linear effects of all the four independent variables, the interaction effect of the adsorbent dosage and initial MBD concentration and the quadratic one of the initial MB concentration and pH significantly impacted MBD removal (*P*-values<0.05; *F*-values≥8.59). In fact, the lowest the *P*-value and the highest the *F*-value, the most significant is an effect [42]. Finally, the overall model was significant and suitable to describe the experimental data having a *P*-value<0.0001 and a R^2 as high as 0.968.

To find the optimum conditions, the optimization criteria selected in the software were: initial concentration, pH, adsorbent dosage and contact time: 'inrange'; and response: 'maximize'. Accordingly, the predicted maximum MBD removal was found to be 84.85% with desirability of 0.85 under the following conditions: adsorbent dosage of 2.5 g/L, pH 9.0, contact time of 138.65 min, and initial dye concentration of 43.75 mg/L.

6. Desorption Tests

Desorption studies are necessary to complete the investigation of the mechanism involved in the adsorption of an adsorbate by an adsorbent as well as to regenerate the adsorbent for economic success. In the present study, desorption was explored, varying the pH from 5.0 to 9.0 and, keeping constant the adsorbent dosage at 2.5 g/L. A decrease in pH favored MBD desorption from CZC because of electrostatic repulsion between positively charged sites on the adsorbent surface and cationic dye molecules [2,3]. The feasibility of using CZC in successive adsorption-desorption cycles was examined by contacting 25.00 mg/L MBD solution with 2.0 g/L recycled adsorbent at pH 9.0. Under these conditions, MBD removal by CZC and recycled CZC was 95.8% and 68.4%, respectively. Such a marked loss of sorption capacity suggests that reuse of desorbed CZC would need some regeneration before recycling.

CONCLUSION

Shrimp waste, a by-product of food processing, was used to pre-

Table 6. Results of response surface methodology and analysis of variance applied to MBD removal by chitosan/zeolite composite

Source	Coefficient	Sum of squares	Degree of freedom	Mean square	*F*-value	*P*-value
Model	b_0 43.40	7898.66	14	564.19	32.09	<0.0001
Contact time (x_1)	b_1 2.54	154.75	1	154.75	8.8	0.0096
pH (x_2)	b_2 3.25	253.69	1	253.69	14.43	0.0017
Adsorbent dosage (x_3)	b_3 9.41	2126.27	1	2126.27	120.93	<0.0001
Initial MBD concentration (x_4)	b_4 −12.25	3602.9	1	3602.9	204.92	<0.0001
x_1x_2	b_1b_2 0.98	15.3	1	15.3	0.87	0.3657
x_1x_3	b_1b_3 −0.55	0.049	1	0.049	0.002781	0.9586
x_1x_4	b_1b_4 −1.14	20.83	1	20.83	1.18	0.2936
x_2x_3	b_2b_3 −0.67	7.14	1	7.14	0.41	0.5335
x_2x_4	b_2b_4 −0.47	3.48	1	3.48	0.2	0.6628
x_3x_4	b_3b_4 −3.07	150.97	1	150.97	8.59	0.0103
x_1^2	b_1^2 −0.39	4.1	1	4.1	0.23	0.6362
x_2^2	b_2^2 3.42	321.67	1	321.67	18.3	0.0007
x_3^2	b_3^2 −0.60	10.39	1	10.39	0.59	0.454
x_4^2	b_4^2 6.74	1232.18	1	1232.18	70.08	<0.0001
Residual		263.73	15	17.58		
Lack of fit		260.45	10	26.04	39.63	0.0004
Pure error		3.29	5	0.66		
Cor total		8162.39	29			

pare a low-cost composite material with zeolite (CZC) as an adsorbent to remove the cationic methylene blue dye (MBD). The experimental results of adsorption tests performed according to a central composite design were worked out by response surface methodology. A quadratic model allowed correlating the independent variables, namely the contact time, pH, initial dye concentration and adsorbent dosage, to the MBD removal selected as a response. The results of ANOVA showed that all the process variables exerted significant effects on the response. Optimum conditions able to maximize MBD removal (84.85%) were found to be a contact time of 138.65 min, pH 9.0, an initial dye concentration of 43.75 mg/L, and adsorbent dosage of 2.5 g/L. The pseudo-second order and Langmuir models were shown to be the best kinetic and isotherm models able to describe MBD adsorption onto CZC. The results of this study demonstrated that the CZC could be used as a low cost adsorbent for removal of dyes from industrial wastewater.

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